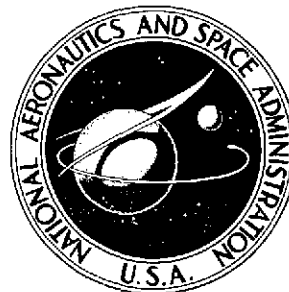


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ELECTRICAL RESISTIVITY OF SOME PALLADIUM-SILVER ALLOYS CONTAINING HYDROGEN AT 4.2 K

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ELECTRICAL RESISTIVITY OF SOME PALLADIUM-SILVER ALLOYS

CONTAINING HYDROGEN AT 4.2 K

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SUMMARY

The change in the electrical resistivities and lattice parameter of the palladium (Pd) - silver (Ag) alloys 90Pd-10Ag, 80Pd-20Ag, 70Pd-30Ag, 60Pd-40Ag, and 50Pd-50Ag were studied as functions of hydrogen content. (All nominal alloy compositions are in atom percent.) The electrical resistivity at 4.2 K as a function of the hydrogen-palladium atom ratio x plots show minimum and maximum values. (The 90Pd-10Ag alloy showed only a maximum, and 50Pd-50Ag showed only a minimum.) These results are qualitatively explained in terms of the model proposed by Bambakidis, Smith, and Otterson (ref. 1) for the palladium-deuterium system and a modified palladium d-band. The palladium d-band modification is associated with hydrogen-hydrogen, hydrogen-palladium, and palladium-silver-hydrogen interactions. Two lattice constants are observed for the alloys, 90Pd-10Ag, 80Pd-20Ag, and 70Pd-30Ag, for hydrogen-palladium atom ratios up to approximately 0.52, 0.35, and 0.20, respectively. The observed crystal structures were face centered cubic (fcc), and the difference in the lattice constants decreased with increasing silver content. The lattice constant data were obtained at approximately 295 K.

INTRODUCTION

The electrical resistivity ρ of palladium (Pd) arises from s-s and s-d scattering of the conduction electrons (ρ_{ss} and ρ_{sd} , respectively). For palladium $\rho_{sd} \gg \rho_{ss}$ (ref. 2, pp. 265-269). In the palladium-hydrogen and palladium-silver systems, the hydrogen (ref. 2, p. 200) or silver s-electrons are assumed to fill the holes in the palladium 4d band (ref. 2, pp. 297-302). This decreases the number of empty d-sites into which the palladium conduction electrons may be scattered. Therefore, the contribution

of ρ_{sd} to the resistivity should decrease. But, both systems (Pd-H and Pd-Ag) show increases in resistivity as the Pd d-band is filled.

In the palladium-silver system the silver ion is substitutionally alloyed into the fcc palladium lattice; this alters the lattice potential and increases ρ_{ss} markedly (ref. 2, pp. 296-302). But in the palladium-hydrogen system the hydrogen occupies the octahedral (interstitial cube edge) sites of the face centered cubic (fcc) palladium lattice as strongly screened ions (ref. 1) and may not effectively scatter the conduction electrons. The increase in the resistivity with increasing hydrogen-palladium atom ratio, x , is therefore more difficult to understand. Two phases, α and β , can be formed up to approximately 573 K. Both are fcc with the hydrogen ions in the octahedral sites. The lattice parameters of the α - and β -phases at room temperature are approximately 3.895×10^{-10} and 4.025×10^{-10} meter (3.895 and 4.025 Å) respectively. The α -phase exists for $x \leq 0.015$; α - and β -phases coexist for $0.015 < x < 0.6$; and only the β -phase is found for $x > 0.6$ (ref. 3, pp. 29, 123, 142, and 143).

A study of the resistivity of the ternary system palladium-silver-hydrogen, however, does show features that lead to additional understanding of processes controlling the resistivity of Pd alloys (refs. 4 and 5). Some of these results show an initial decrease in the resistivity when hydrogen is first added. This is what could be expected if the hydrogen electron starts to fill the d-band, thereby decreasing the s-d scatter of the conduction electrons. As the hydrogen content increases, ρ eventually increases showing that another scattering mechanism becomes dominant. Evidently, several processes are active when the palladium d-states are being filled.

In this report, we measure the structural resistivities of the palladium-silver (Pd-Ag) alloys 90Pd-10Ag, 80Pd-20Ag, 70Pd-30Ag, 60Pd-40Ag, and 50Pd-50Ag containing hydrogen at 4.2 K to obtain the temperature independent contribution. (All alloy compositions are in atom percent.) We then compare these results with our data taken at 273 K, the data taken by Carson, Lewis, and Schurter at 298 K (ref. 6), and that by Sieverts and Hagen at "155-484°" (ref. 5). Our results are qualitatively explained in terms of a modification of the palladium d-electron population due to the presence of silver and hydrogen. The concepts of s-d scattering of conduction electrons and the screening theory of Bambakidis, Smith, and Otterson (ref. 1) are used.

EXPERIMENTAL

The resistivity samples used were in wire form of 0.267 millimeter diameter. The alloys were 90Pd-10Ag, 80Pd-20Ag, 70Pd-30Ag, 60Pd-40Ag, and 50Pd-50Ag. The analyses of the wires are shown in table I. The manufacturer's stated purities were 99.99+ atomic percent palladium and 99.999 atomic percent silver before alloying. The wires

were annealed at 1023 K in a vacuum of 8×10^{-7} newton per square meter (6×10^{-9} torr) for 2 hours.

Hydrogen was introduced into the alloys electrolytically in a 0.1 N sulphuric acid and sodium sulfide solution. The charging current density was approximately 8 milliamperes per square centimeter. The charging times varied from 2 to 120 minutes, depending on the hydrogen content desired.

The resistivity measurements were made before and after hydrogen absorption for each wire by the standard four-probe potentiometric technique using a constant current dc source of 10 milliamperes and a standard resistor. The test temperatures were 4.2 K (liquid helium) and 273 K (ice water). Resistivity measurements were made on three adjacent sections of each wire. Each section was approximately 1 centimeter long. In this way we were able to estimate the hydrogen distribution along the wire.

Immediately after the resistivity measurements the specimens were immersed in liquid nitrogen until they could be weighed and placed in the desorption chamber. Storage in liquid nitrogen prevents hydrogen loss (ref. 7). The elapsed time between removal from the liquid nitrogen and desorption in the mass spectrometer did not exceed 10 minutes. The hydrogen was desorbed at 870 K. The hydrogen content is expressed herein in the form of the hydrogen-palladium atom ratio x . The accuracy of the determination is within 1 percent of the values shown. A hydrogen determination was made for each centimeter section of wire for which a resistivity measurement was obtained.

Separate specimens were used for lattice parameter measurements. This permitted the lattice parameter to be plotted against x . It took 8 to 16 hours to obtain these measurements. Therefore, we attempted to determine the effect of hydrogen loss on the measurements for the 8- to 16-hour period. After obtaining one set of X-ray powder patterns in an 8- or 16-hour run, the same specimens were rerun the following day without being removed from the camera. The hydrogen analyses were made just before the first run and immediately after the second run.

RESULTS

Figure 1 shows the changes in the shape of ρ/ρ_0 as a function of x as the silver content is increased from 90Pd-10Ag to 50Pd-50Ag in 10 atomic percent increments at 4.2 K. (ρ_0 is the resistivity of the alloy before hydrogen absorption and ρ is the resistivity after hydrogen absorption.) The maximum in ρ/ρ_0 as a function of x for pure palladium occurs for $x \approx 0.77$. As silver is added, this maximum tends to move to lower values of x . No maximum was found for 50Pd-50Ag for $x \leq 0.54$. A minimum in ρ/ρ_0 as a function of x is first seen in 80Pd-20Ag for $x \approx 0.3$ to 0.4. For increasing silver content, this minimum also moves to lower values of x . The minimum is still observed in 50Pd-50Ag for $x \approx 0.07$. No minimum occurs when silver content exceeds

55 atomic percent (ref. 6). An initial increase followed by a decrease in ρ/ρ_0 as a function of x is observed for 80Pd-20Ag and 70Pd-30Ag. The plots of these results are similar to those of references 4 to 6. We do not present our data at 273 K because it is quite similar to the 4.2 data and our present interest is in the structural resistivity.

In figure 2 the lattice parameter, a_0 , increases linearly with silver content in palladium. However, the alloys show a slightly smaller lattice parameter than would be expected by Vegard's law, thus indicating increased electron overlap (ref. 8). In figure 3 a_0 is plotted against x for each alloy. The alloys 90Pd-10Ag, 80Pd-20Ag, and 70Pd-30Ag show double values of a_0 for $x < 0.5$. At $x \sim 0.1$ the 70Pd-30Ag alloy shows three values for a_0 on one specimen. Reference 3 indicates that the two-phase region for the Pd-Ag-H system exists up to a silver content of approximately 27 atomic percent. The analysis of our 70Pd-30Ag alloy shows values of 26.81 and 29.00 atomic percent silver. The first value could still show two phases while the second value is in the single-phase region for the palladium-silver-hydrogen system. This would account for our triplet value of lattice parameter for the 70Pd-30Ag alloy.

In general, our results show the lattice parameter increasing with x for all the alloys in the single-phase regions. But in the two-phase regions the values of the lattice parameter remain rather constant until the systems become single phase again.

The results of our attempt to check the changes in lattice parameters due to hydrogen desorption while standing in air are inconclusive. The work does show that large concentrations of hydrogen in the palladium-silver alloys are unstable (at room temperature). The arrows in figures 3(b), (c), and (e) point to the initial and final values of x for a given specimen. In figure 3(b) one specimen was initially charged to $x = 0.268$ with a lattice parameter of 3.9299×10^{-10} meter (3.9299 Å). However, after standing in air at room temperature, the second measurement of the lattice parameter shows two distinct values: 3.9337×10^{-10} and 3.949×10^{-10} meter (3.9337 and 3.9492 Å). The final value of x was 0.145. The initial (a) and final (b) values of the lattice parameter are indicated by the "branched" line. We suggest that in the initial X-ray measurement the second lattice parameter was too weak to be detected. In any case, there is a large uncertainty in the lattice parameter since the X-ray data take at least 8 hours per specimen and desorption is occurring during the measurements. Whether or not a hysteresis exists cannot be determined from these measurements.

DISCUSSION

It is now generally agreed that pure palladium has approximately 0.36 d-band hole per atom. This has been determined by deHaas - van Alphen experiments (ref. 9). Before the deHaas - van Alphen experiments, the electrical resistivity (ref. 2) and magnetic susceptibility χ (ref. 10) results were interpreted in terms of palladium having

0.52 to 0.6 d-hole per atom. In the palladium-silver system the curvature in the plot of χ as a function of the amount of silver (in at. %) in palladium was interpreted as showing the variation of the density of states $N(E)$ at the Fermi level E_F ; that is,

$$\frac{d^2N(E)}{dy^2} \neq 0$$

where y is the amount of silver (in at. %) in palladium. The plot shows a gentle curvature that can be approximated by $N(E) \propto (0.55 - y)^2$ (ref. 2, p. 199). This variation in $N(E)$ at E_F could account for the apparent 0.55 d-hole, instead of a 0.36 d-hole, per palladium atom. In the χ as a function of x data, $\chi = 0$ for $x \approx 0.6$, which implies a 0.6 d-hole per palladium atom. But the plot appeared to be linear for $0 \leq x \leq 0.6$ (ref. 2, p. 200).

However, this is a two-phase system, except for $0.015 > x > 0.6$. Eastman, Cashion, and Switendick (ref. 11), in their photoemission studies of hydrogen in palladium, reconcile the difference between the deHaas - van Alphen work (0.36 d-hole) and the hydrogen in palladium susceptibility work. They suggest that the absorbed hydrogen first forms hybridized states with the existing palladium d-states; this results from hydrogen-palladium interactions. These states strongly screen the hydrogen ions. Then previously unoccupied 5sp-states are pulled below the Fermi surface E_F and the top of the d-band. These 'new' low lying sp-states result primarily from hydrogen-hydrogen interactions. The hydrogen electron fills both the originally empty 4d-states and the new 5sp states. This accounts for the apparent 0.6, instead of the 0.36, d-hole filling.

Recent susceptibility work by Frieske and Wicke (ref. 12) does show two nonlinear portions on the χ as a function of x plot at 293 K. The first nonlinear portion occurs for $0 \leq x < 0.015$. For $0.015 \leq x \leq 0.6$ ($\alpha + \beta$ region), the plot is linear (i. e., $dN(E)/dx = \text{constant}$). This linear portion passes through $\chi = 0$ at $x \approx 0.6$ implying 0.6 d-hole per palladium atom. If we associate the nonlinear portion of χ as a function of x with a variation in $N(E)$ at E_F , we can assume that $N(E)$ at E_F varies more rapidly per initial hydrogen atom addition than it does per silver atom addition; moreover, from the initial slope of the χ as a function of x plot (ref. 12), we can assume

$$\frac{d^2N(E)}{dx^2} > \frac{d^2N(E)}{dy^2}$$

It is the initial rapid variation in $N(E)$ per hydrogen atom addition with which we associate the sharp increase in ρ/ρ_0 when plotted against x . However, the slope of ρ/ρ_0 against x decreases as the silver content in palladium increases (as the volume

difference between α - and β -phases Δv decreases, $d(\rho/\rho_0)/dx$ decreases). Moreover, the silver atom modifies $N(E)$ and the additional modification due to the hydrogen atom is less pronounced. For those alloys that have a mixed-phase region ($\alpha + \beta$), the resistivity is merely the average of $\rho_\alpha + \rho_\beta$. The α - and β -phases coexist for certain values of x for palladium-silver alloys up to 27 atomic percent silver at 293 K (ref. 13). As the silver content is increased beyond 27 atomic percent, the remaining modification is further reduced; that is, $d^2N/dx^2 \rightarrow 0$. And the primary effect of hydrogen absorption is merely filling the remaining electron holes below E_F . This is most clearly seen in the 60Pd-40Ag and 50Pd-50Ag alloys; ρ decreases initially on hydrogen absorption. This should be the case if the only effect is to decrease the number of empty d-type states below E_F into which s-electrons may be scattered along with strong screening of the hydrogen ion.

We assume the filling of the d-band occurs at the end of the two-phase region (fig. 3) for the 90Pd-10Ag, 80Pd-20Ag, and 70Pd-30Ag alloys. This occurs beyond the minimum for the 80Pd-20Ag and 70Pd-30Ag alloys. In fact, the filling occurs as ρ/ρ_0 is increasing rapidly with increasing x as was discussed for the palladium-deuterium and palladium-hydrogen systems (refs. 1 and 7). As assumed by Bambakidis, Smith, and Otterson, when the d-band is almost filled, the contribution by ρ_{s-d} to ρ is small, and the additional hydrogen ions are less well screened. The increase in ρ is attributed to ρ_{ss} involving the less well screened hydrogen ions and hydrogen vacancies in the interstitial octahedral sites. We assume the filling of the d-bands of 60Pd-40Ag and 50Pd-50Ag alloys also occurs beyond the minimum of the ρ/ρ_0 as a function of x curve and in the region where ρ/ρ_0 increases rapidly. The subsequent maxima indicate that periodicity in the hydrogen lattice is taking effect (hydrogen vacancies are being filled) and that ρ/ρ_0 will decrease as x increases.

From these results it appears that the effect of decreasing the d-band hole concentration at E_F by "implanting extra electrons" can be registered as a decrease in electrical resistivity through a decrease in s-d scatter of conduction electrons. For silver contents in excess of 27 atomic percent, the β phase does not appear. (Evidently, the hydrogen ion is more easily accommodated in the larger lattice.) We suggest the presence of the silver atom weakens the hydrogen-hydrogen interaction and, to some extent, the hydrogen-palladium interactions.

CONCLUSIONS

1. The decrease in $(d/dx)(\rho/\rho_0)$ in the α -phase, with increasing silver content is due to the modification of the Pd d-band (i. e., $d\rho_\alpha/dx$ decreases as the silver content increases).

2. As $d\rho_\alpha/dx$ decreases with increased silver content (the mixed phase region, $\alpha + \beta$) a subsequent decrease in ρ/ρ_0 is observed. This is associated with ρ_β being small due to its filled d-band (no s-d scatter) and initially well screened hydrogen ion.

3. In the single-phase palladium-silver (Pd-Ag) systems, such as 60Pd-40Ag and 50Pd-50Ag, the initial decrease in ρ/ρ_0 due to hydrogen addition is caused by the relatively simple filling of the palladium d-band. (The remaining modification of the Pd d-band is considered small at these silver contents.)

4. The subsequent increase in ρ/ρ_0 , in all the alloys, with increasing hydrogen content is caused by the s-s contribution to the resistivity associated with the less well screened hydrogen ion.

5. The maximums observed at high hydrogen contents arise from decreased disorder scattering as the hydrogen lattice fills.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, February 27, 1974,
502-01.

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TABLE I. - ANALYSIS OF

PALLADIUM-SILVER

ALLOYS

| Alloy designation | Silver content, at. % (a) |
|---------------------------------|------------------------------|
| Pd ₉ Ag ₁ | 9.79, 9.60 |
| Pd ₈ Ag ₂ | 20.02, 19.81 |
| Pd ₇ Ag ₃ | 26.81, 29.00 |
| Pd ₆ Ag ₄ | 38.22, 38.99 |
| Pd ₅ Ag ₅ | 50.72, 50.05 |

^aThe results are from two samples of each alloy.

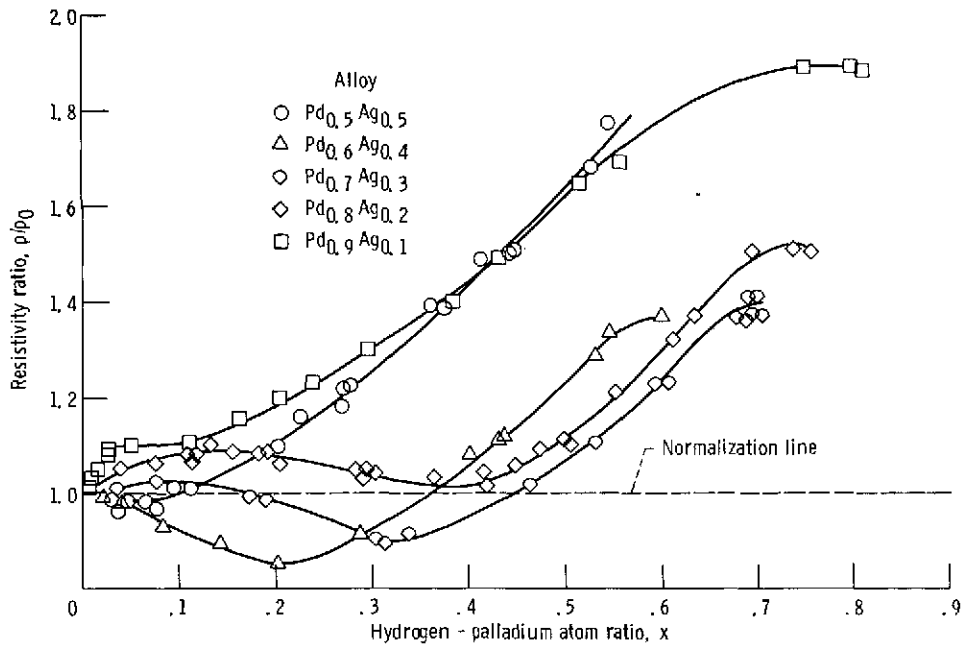


Figure 1. - Resistivity ratio as function of hydrogen palladium atom ratio for palladium-silver (Pd - Ag) alloys at 4.2 K.

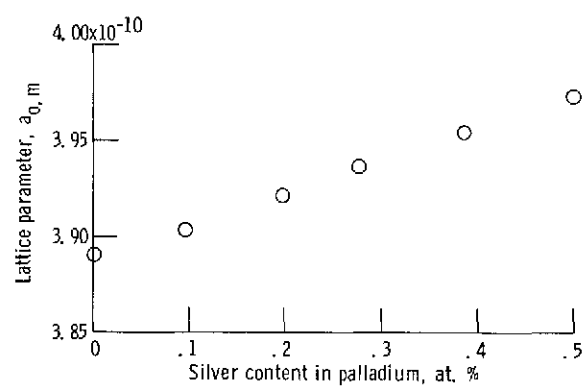


Figure 2. - Lattice parameter as function of increasing silver content in palladium.

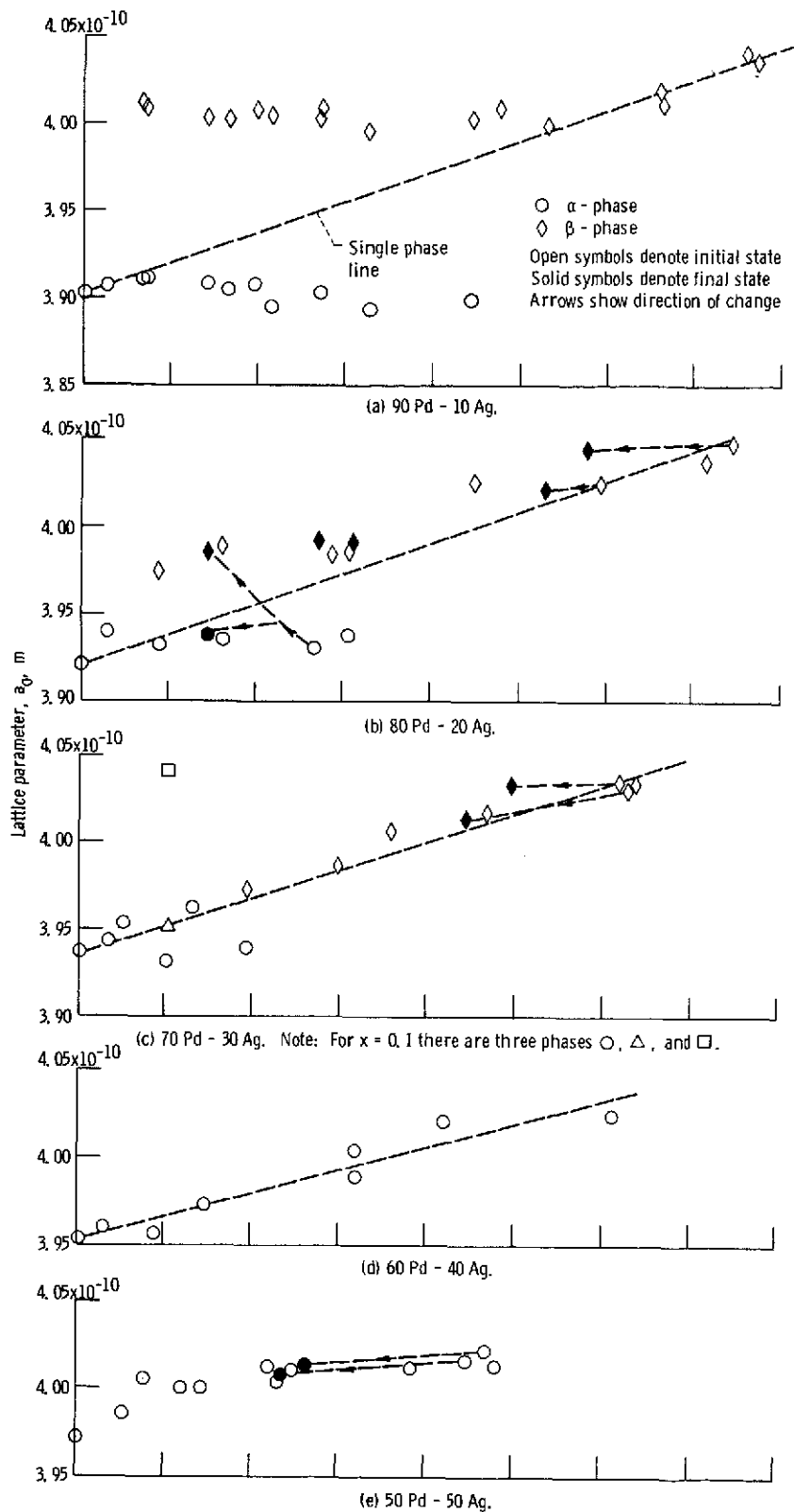


Figure 3. - Lattice parameter as function of hydrogen-palladium atom ratio in palladium-silver alloys.